

## **Development of an *In-Situ* Mass Spectrometer for Stable Isotope Analyses**

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### **LONG-TERM GOALS**

Long-term goals for this project are to extend the use and application of small portable in-situ isotope ratio mass spectrometers for studies of a wide range of dissolved chemical species, including various forms of dissolved inorganic and organic carbon. Isotopic assessment of dissolved species can lead to the development of predictive tools for determining the biological-physical response of coastal oceans to natural climatic and anthropogenic changes, and to the seasonal development of physical boundary conditions (e.g., particle density distributions and perturbations in light transmittance).

### **OBJECTIVES**

During this funding cycle, a mini-magnetic sector mass spectrometer from Intelligent Ion, Inc. (Seattle, WA) was to be constructed, delivered to USF and integrated into a laboratory membrane-introduction vacuum system for evaluation and methods development. The mass spectrometer was to come equipped with a 16-element detector array placed at appropriate positions for analysis of low-molecular weight gases (e.g., N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub>). Initially, the mass spectrometer was to be configured and tested under controlled conditions on the lab bench using standard gases introduced directly into the instrument. System performance (precision and accuracy) of <sup>13</sup>C/<sup>12</sup>C measurements for dissolved and gas-phase CO<sub>2</sub> was to be evaluated using gas standards, isotopically-calibrated CO<sub>2</sub> reference gases and acidified reference sea water samples. Coulometric measurements of dissolved inorganic carbon (DIC) were also to be obtained for comparison with the mini-sector mass analyzer results. Using this approach we should be able to accurately determine not only instrument precision and accuracy but also sensitivity and linearity, thereby constraining the range of possible applications.

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## APPROACH

High precision measurements of stable isotope ratios are almost exclusively performed in the laboratory on large magnetic sector mass spectrometers. The most precise measurements of this type are made using sector mass spectrometers that simultaneously detect isotopes of interest.

Simultaneous detection using a sector mass spectrometer is the superior method for precise isotope measurements for a number of reasons: 1) the electronics required for this type of mass analyzer are simple, allowing a high degree of stabilization; 2) the duty cycle for each isotopic species is increased to essentially 100%; and 3) any fluctuations in instrumental parameters affect all mass intensity measurements, thereby nullifying effects on mass ratios. The highest absolute accuracy isotope ratio measurements are obtained using instruments of this type that also allow periodic comparison of measured sample ratios with standards of known isotopic composition.

While no commercially available *portable* sector mass spectrometers for simultaneous isotopic monitoring have been developed to date, Intelligent Ion, Inc. (Seattle, WA) is very close to producing a miniature magnetic sector mass spectrometer<sup>1,2</sup> with this facility. Their mass spectrometer, based on the Mattauch-Herzog design<sup>3,4</sup>, is ideal for simultaneous detection, as it provides a linear double focus (angle and energy) over a very large mass range. The Intelligent Ion, Inc design effects double focusing by placing a series of individual microfabricated Faraday cup detectors along the linear focal plane<sup>5,6</sup>. For our application, we propose a design that will allow monitoring of up to 16 individual masses, so that *each molecular weight of interest will have its own detector element*. In addition, Intelligent Ion, Inc. has developed highly sensitive and rapid readout electronics coupled with each microfabricated detector element, resulting in satisfactory detection limits and a nearly 100% duty cycle for all monitored masses.

## WORK COMPLETED

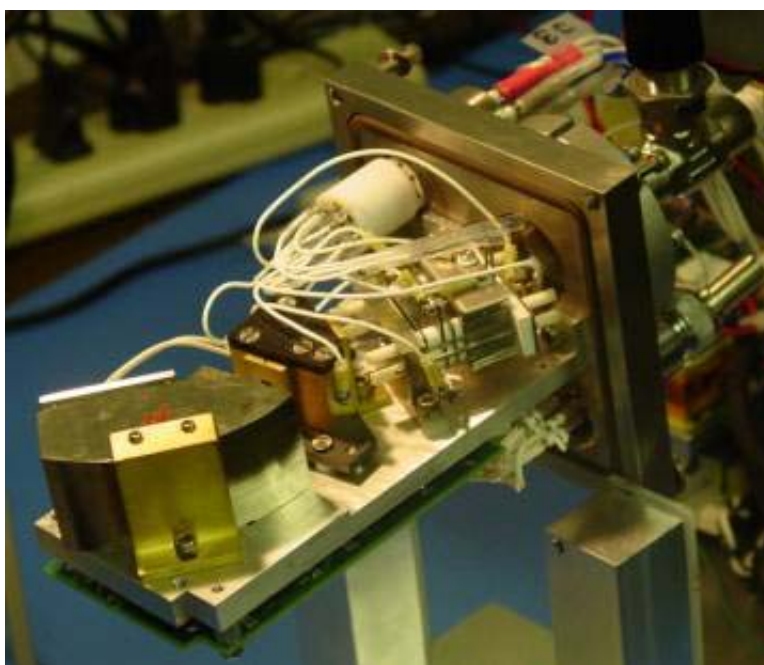
The primary component required for development of the proposed in-situ instrument is the mini magnetic sector mass spectrometer, to be provided by Intelligent Ion, Inc. Delivery of this instrument is expected in early October, 2002. University of South Florida (USF) personnel have been involved with final design and testing of the instrument to ensure compatibility with proposed applications. Two members of the USF project team visited the Intelligent Ion, Inc. facility in Seattle, WA in late April, 2002. At that time it was decided to replace the proposed 16-cup Faraday cup array with a 100-cup array. This change delayed the delivery of the system by a couple of months, but will dramatically enhance the capability and flexibility of the instrument. At this time the vacuum system for the mass spectrometer had been assembled and tested (Figure 1).

The vacuum system/computer subassembly was delivered to USF in June 2002 in order to allow USF personnel to evaluate the compatibility of the vacuum system with the membrane introduction sampling system, and to allow familiarization with the instrument control software. This also allowed USF to identify potential changes to subsystems that might be required for proposed applications. The subsystem was then returned to Intelligent Ion, Inc. for installation of the mass spectrometer components shown in Figure 2. After return of the vacuum system/computer subassembly to III, the mini-sector mass spectrometer (with the 100-Faraday cup detector array) has been installed into the vacuum system. Initial tests have been completed and optimization of the ion source parameters is in progress.

Components for the automated in-line acidification system have been ordered (and partially received), and a preliminary design for the in-line acidification system has been devised. A gas acidification module, which will be used to perform benchmark measurements on a much larger laboratory isotope ratio mass spectrometer, has also been ordered.



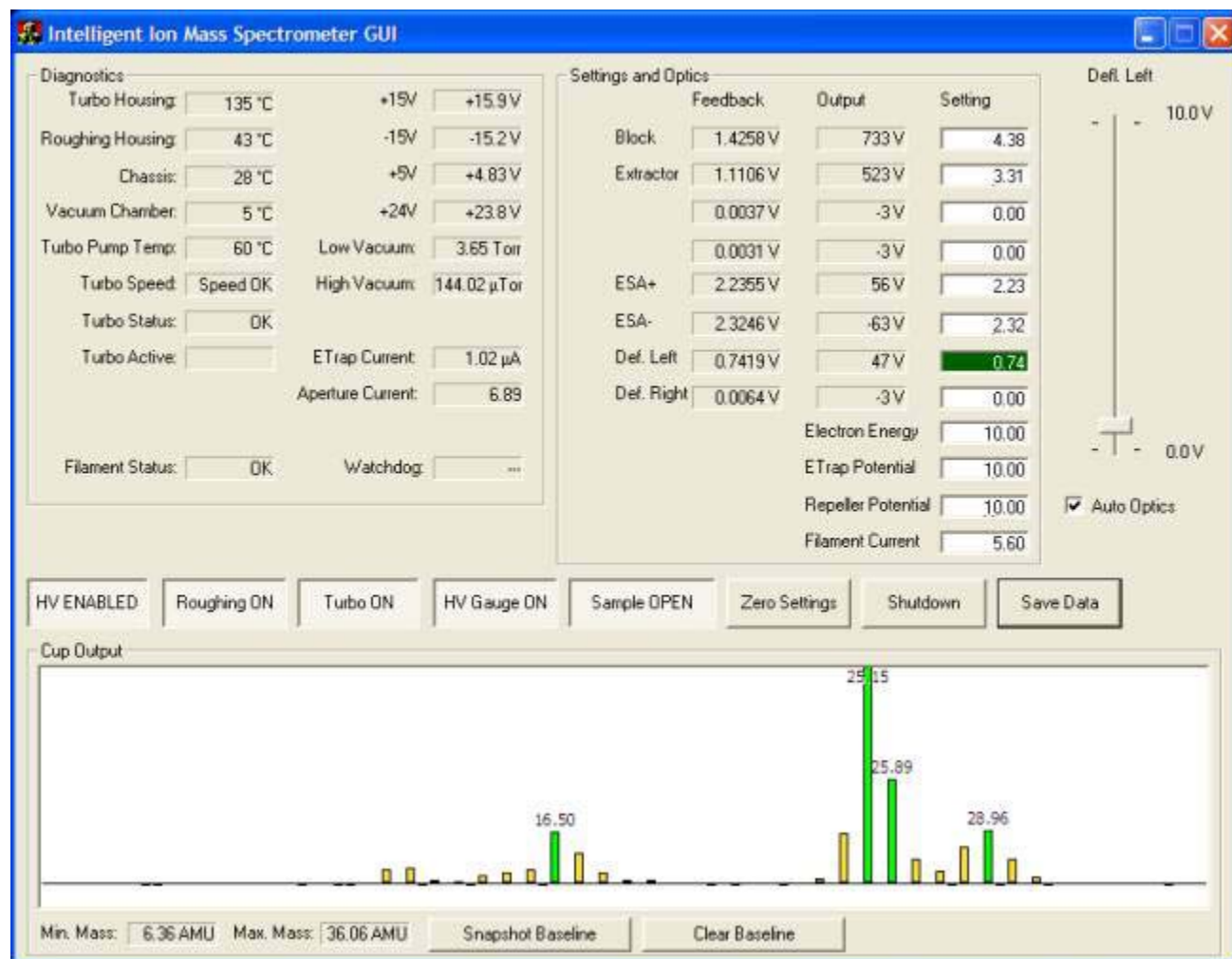
*Figure 1. Vacuum system for the III mini-sector mass spectrometer.*



*Figure 2. Mini-magnetic sector mass spectrometer with 100-Faraday cup array.*

## RESULTS

Intelligent Ion Inc. personnel have integrated the mini-magnetic sector mass spectrometer with the 100-Faraday cup detector array to produce a truly unique and flexible analyzer with essentially a 100% duty cycle for a wide range of masses. The first spectrum obtained from this device is shown in Figure 3 below.



**Figure 3.** Mass spectrum of background gases in the miniature sector mass spectrometer obtained using a 100-Faraday cup detector array. Acquisition time was approximately 50 msec.

## IMPACT/APPLICATIONS

The ability to perform in-situ isotopic analyses should have a profound impact on data acquisition rates. Rapid in-situ isotopic analysis should significantly advance capabilities to measure and model rapidly varying dynamic biogeochemical processes in the oceans and atmosphere. In addition to oceanic applications, a small portable mass spectrometer of this construction, with a 100% duty cycle

and a broad mass range, should have broad high-value applications for both scientific and regulatory purposes.

## RELATED PROJECTS

This project is a direct spin off from another ONR funded proposal “Development and Deployment of In-Situ Mass Spectrometers” Grant Number: N00014-98-1-0154.

## REFERENCES

1. Sinha, M.P. and A.D. Tomassian (1994) Miniaturized lightweight magnetic sector for field-portable mass spectrometer. *U.S. Patent* 5,317,151.
2. Scheidemann, A.A., K.E. Robinson, S.C. Gottschalk and P. Jones (1998) Magnetic sector for linear dispersion and method for producing same. *U.S. Patent filed* 10/06/98.
3. Mattauch, J. and R. Herzog (1934) *Zeits. f Physik* **89**, p786.
4. Mattauch, J. (1936) A double-focusing mass spectrograph and the masses  $N^{15}$  and  $O^{18}$ . *Phys. Rev.* **50**, pp. 617-623.
5. Darling, R.B., A.A. Scheidemann, K.N.Bhat and T.C. Chen (2001) Micromachined Faraday cup array using deep reactive ion etching. *Proceedings of the 14<sup>th</sup> International Conference on Micro Electro Mechanical Systems (MEMS)*. January 21-25, 2001, Interlaken, Switzerland, pp. 90-93.
6. Darling, B., A.A. Scheidemann and F.J. Schumacher (1999) Faraday cup detector array with electronic interface. *Provisional U.S. Patent filed* 01/22/99.